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# Hydrogeochemical investigations of an abandoned uranium mine in the Erzgebirge/Germany

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**Abstract**—The detrimental environmental effects of the eastern German U mines resulted in a close down of all the mines. With a depth of nearly 1800 m, the Niederschlema/Alberoda mine was the first one to be flooded. Statistical investigations and thermodynamic calculations with WATEQ4F revealed that the mine water's constituents reached a local maximum. Copyright © 1996 Elsevier Science Ltd

## INTRODUCTION

The years 1989 to 1991 meant the end of the Soviet predominance in the eastern German U mining industry. While the Soviet scientists and managers of the SDAG Wismut, the company who operated the mines, left, the remnants of nearly half a century of U mining remained.

On 3rd October 1990 the Federal Ministry of Economic Affairs, due to the German Reunification, were given the responsibility of 50% of the eastern German U mines in Saxonia and Thuringia. After a contract with the Soviet Government on 16th May 1991 the Federal Republic of Germany also took over the Soviet shares of the SDAG Wismut (Bundesministerium für Wirtschaft, 1993).

Of the 250 kt of $UO_2$ that were mined by the Wismut until 1990 nearly 40% came from the hydrothermal Niederschlema/Alberoda deposit (Lange *et al.*, 1991). After the U.S.A. and Canada the Wismut was the third largest U producer in the world (Bundesministerium für Wirtschaft, 1993).

Because of the low price for yellow cake at the end of the 1980s and the negative impact on the environment, the E German government decided to stop the U mining on 31st December 1990. Nevertheless Germany produced 3000 t of U in 1990 (Lange *et al.*, 1991; Bundesministerium für Wirtschaft, 1993).

The Niederschlema/Alberoda U deposit is situated approximately 40 km SW of Chemnitz, in the Saxonian Westerzgebirge (Western Ore Mountains) near the townships of Schlema and Aue (Fig. 1). In
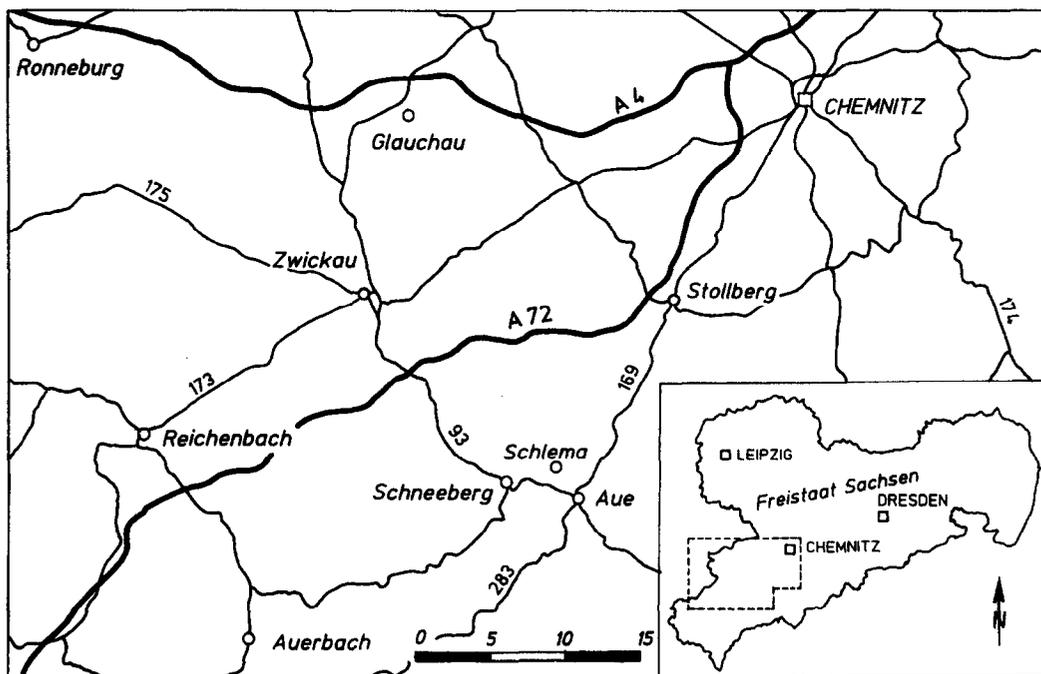


Fig. 1. Map of the central Erzgebirge SW of Chemnitz.

this paper the mine's hydrogeochemistry will be discussed and some conclusions will be presented.

## LOCAL GEOLOGICAL CONDITIONS

The Erzgebirge is part of the Variscan orogenic belt and belongs to the Saxothuringian zone (Walter *et al.*, 1992). Low to high grade metamorphized rocks, granites, and some metabasites are the most common rocks that occur on the surface.

Situated in a NE–SW striking isoclinal folded syncline, called the Lößnitz–Zwönitz-Syncline, the main rocks of the deposit are slightly metamorphized Palaeozoic rocks of Ordovician, Silurian and Devonian age. In the contact aureole of the Aue Granite the rocks are contact metamorphized and accompanied by young, non-metamorphic aplites and kersantites. The Aue granite itself belongs to the Older Intrusive Complex (OIC) of the Erzgebirge (SDAG Wismut, 1991).

In the Erzgebirge the hydrothermal mineralization with more than 140 reported minerals (Schröder and Lipp, 1990a,b) is divided into 6 "formations" (formation nowadays is a stratigraphic term; in the context of the Erzgebirge ore formations it is commonly used in the sense of "type of ore vein"), which are shown in Table 1 (after SDAG Wismut, 1991; Harlass and Schützel, 1965). For the U mineralisation the KKu and mgu formations were the predominant ore veins. In contrast, the arsenides were abundant in the biconi and ags formations

(Harlass and Schützel, 1965; Janischewskij and Konstantinow, 1962). Very important for the hydrogeochemistry of the flooding water are, due to their ability to buffer acid mine drainage, the carbonates that are abundant in most of the ore formations and in the Palaeozoic rocks.

## SAMPLING AND ANALYTICAL METHODS

On 11th January 1991 the pumping of the mine water was stopped and the flooding of the mine began. Since then weekly analyses of the flooding water and the infiltration water have been made (Table 2). The sample sites of the flooding water were chosen due to the available man power and the safety regulations in different mine shafts. Most of the infiltration water sampling sites are on the −540 m level of the mine, where infiltration waters are collected. Infiltration water in this context is used for water that passed through the fractured zones of the deposit (up to 300 m). Its age is normally weeks to months. In contrast, flooding water is used for water which is in contact with the flooded part of the mine and has an age of up to 4 years now.

Flooding waters are collected 5 to 10 m under the water's surface using a PVC probing-tube which is fastened on a steel wire and handled from the −990 or −540 level. Occasionally samples were taken from 20, 50 and 100 m below the surface. Infiltration waters were directly collected with 1, 2 or 10 l PE containers, depending on the sampling plan.

For both, infiltration and flooding waters, the temperature, pH, conductivity and sometimes the redox potential was measured on site. The samples were neither filtered nor acidified.

Normally the samples were analysed on the next day by ICP-OES, or AAS using the standard methods described in the "Deutsche Einheitsverfahren zur Wasseruntersuchung" ("German standard for water analyses").

Table 1. The ore formations of the Erzgebirge in the order of relative age of veins

| Formation | Vein type | minerals |
|---|---|---|
| qa | Old quartz veins | Sulphides |
| Kb | Quartz-sulphide-veins | Sulphides |
| KKu | Quartz-calcite-veins | U-minerals, sulphides |
| mgu | Dolomite veins | U-minerals, sulphides |
| biconi | Quartz-carbonate-veins | Arsenides, U-minerals, sulphides |
| ags | Sulphide-calcite-veins | Arsenides, sulphides |

Table 2. Selection of major parameters from the water analyses of flooding and infiltration waters in mg $l^{-1}$, Ra in mBq $l^{-1}$, Eh in mV

|  | As | U | Temp. | Cond. | Eh | pH | TDS | Ca | Mg | Na |
|---|---|---|---|---|---|---|---|---|---|---|
| *n* | 474 | 465 | 282 | 324 | 59 | 442 | 303 | 318 | 318 | 208 |
| Mean | 2.7 | 2.0 | 28.1 | 2.22 | 95.7 | 7.4 | 2000.8 | 187.3 | 120.0 | 275.7 |
| St. dev. | 2.7 | 1.2 | 9.6 | 1.21 | 30.1 | 0.5 | 994.3 | 72.6 | 56.4 | 176.2 |

|  | K | Mn | $SO_4^{2-}$ | Cl | $HCO_3^-$ | $NO_3^-$ | $PO_4^{3-}$ | $O_2$ | Ba | Ra |
|---|---|---|---|---|---|---|---|---|---|---|
| *n* | 173 | 176 | 399 | 399 | 312 | 317 | 99 | 196 | 16 | 253 |
| Mean | 27.5 | 2.5 | 786.7 | 96.0 | 665.3 | 5.4 | 3.3 | 6.6 | 0.1 | 1299.4 |
| St. dev. | 15.2 | 1.4 | 430.8 | 59.4 | 388.0 | 3.9 | 2.6 | 5.0 | 0.2 | 1182.1 |

TDS, total dissolved solids; temp., temperature in °C; cond., conductivity in mS cm$^{-1}$; *n*, number of samples; st. dev., standard deviation.

Due to the history of the Wismut 2 laboratories which formerly belonged to the Wismut were used. Laboratory A is in Aue, laboratory C in Chemnitz. Counter checking some analyses at the Technical University of Clausthal showed that the magnitude of the analyses is in the same range.

## RESULTS

### Basic treatments

Infiltration and flooding waters can be distinguished by their chemical characteristics. The Piper-diagram (Fig. 2) reveals that the flooding water is relatively enriched in proportions of $Na^+$, $K^+$ and $HCO_3^{2-}$ compared to infiltration waters.

For calculation and prediction purposes it was necessary to characterise the 2 water types by as few parameters as possible. Empirical studies of scatter diagrams revealed that U, As and Ca mass concentrations can be used for this. The ratios $q_1 = \log(n_U/n_{As})$ and $q_2 = -\log(n_{As}/n_{Ca})$ were determined and it was possible to show that samples with $q_1 < -0.2$ and $q_2 < 2.5$ can be described as flooding waters.

### Statistical investigations

To predict the water's future chemistry time series of 6 major parameters were studied ($SO_4$, $HCO_3$, U, As, Ra, total dissolved solids). Uranium mass concentrations in the flooding water increased from 1.5 mg $l^{-1}$ to 3.5 mg $l^{-1}$ during the first 3 a and stays stable between 3.0 and 4.0 mg $l^{-1}$ now (Fig. 3). This is

in the range reported for U mines with a pH between 5.5 and 7.5 ($<2 \cdot 10^{-5} \ldots 5.3$ mg $l^{-1}$, Fix, 1955). In the infiltration waters U is between 0.5 and 1.0 mg $l^{-1}$, already higher than the world background for U in water (0.006 mg $l^{-1}$), but in the range of U mass concentrations near U deposits, which can reach 2.9 mg $l^{-1}$ (Kočzy et al., 1957). The appropriate redox values are about 400 mV and pH 7.8 for infiltration waters as well as 300 mV and pH 7.1 for the flooding water.

The As mass concentration of the infiltration waters is normally under 0.2 mg $l^{-1}$. For the flooding water it rose to a mean of 7.0 mg $l^{-1}$ during the first 2 a, but has decreased since then to a mean of 4.0 mg $l^{-1}$. It appears that it will remain stable now between 4.0 and 7.0 mg $l^{-1}$.

A similar course can be seen for $HCO_3^{2-}$. Its mass concentration increased during the first 3 a from 200 mg $l^{-1}$ to 1000 mg $l^{-1}$ with a maximum of 1300 mg $l^{-1}$. In the flooding water it stabilised at a mean of 900 mg $l^{-1}$, in the infiltration waters at 190 mg $l^{-1}$. It should be mentioned that there is a strong correlation between the As and $HCO_3^{2-}$ mass concentration which is reported elsewhere (Wolkersdorfer, 1994).

Sulphate mass concentration in the flooding water shows a strong linear trend with time. At the moment it cannot be said with certainty if the $SO_4$ mass concentration has reached its maximum or not. At the beginning of the flooding the $SO_4$ mass concentration was at a mean of 700 mg $l^{-1}$ and it has now reached a mean of 1350 mg $l^{-1}$. As could be seen with the other constituents, $SO_4$ mass concentration in the infiltration waters was stable, at 400 mg $l^{-1}$.
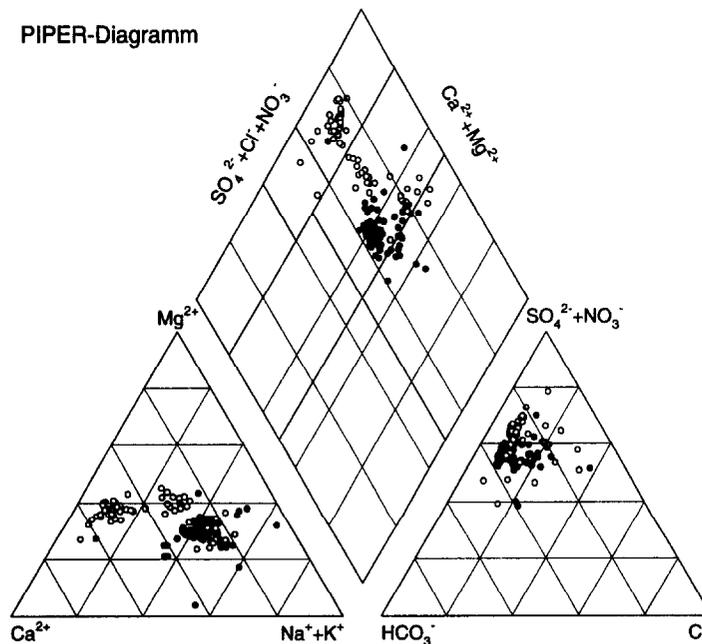


Fig. 2. Piper-diagram of 172 water samples from the Niederschlema/Alberoda U mine. Hollow circles: infiltration waters; closed circles: flooding water.

## Uranium mass concentration against time
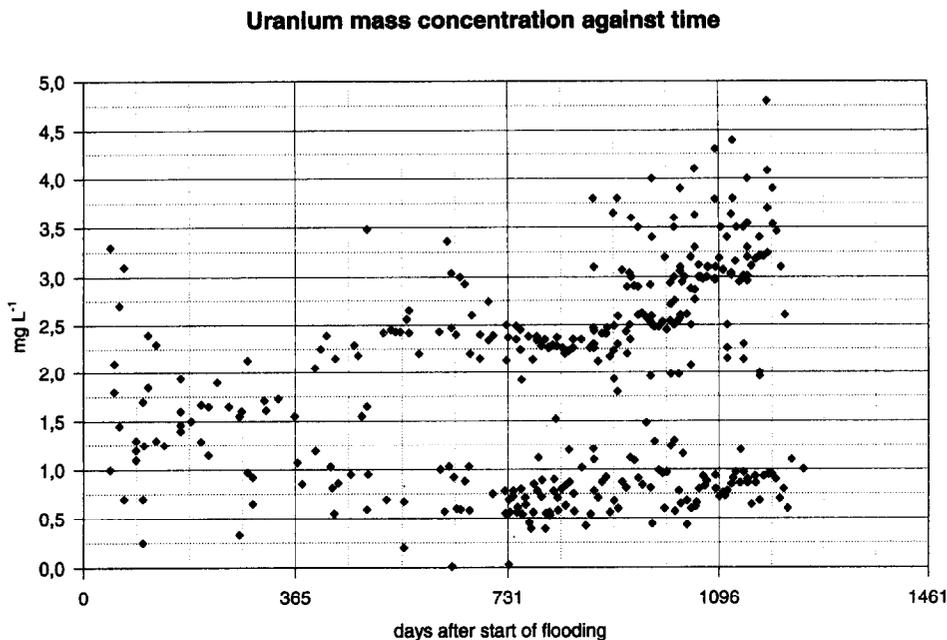


Fig. 3. Uranium mass concentration against time. Infiltration waters and flooding water can be distinguished by the content of U. 398 datapoints.

For Ra an increasing trend could be found, but correlation coefficients are below 0.5. The activity is somewhere between 100 and 3000 mBq l$^{-1}$, the lower values mostly relate to infiltration waters. Compared to the local background the infiltration water has normal activities (Schiffner *et al.*, 1911) whilst the flooding water has significantly higher activities.

An interesting trend occurs in the amount of total dissolved solids. Even if most contents of the constituents Ca, Na, Cl, Mg and HCO$_3$ are nearly stable, the total dissolved solids still increase. While, in the beginning, the water contained 2000 mg l$^{-1}$ it now contains 3000 mg l$^{-1}$. Compared to the infiltration waters, (1000 mg l$^{-1}$), this is 3 times higher.

With the exception of Ra the correlation coefficients for different time — constituent correlations (not only linear) were significantly high (between 0.64 and 0.92) and were used to predict the future mass concentrations within a short time interval.

### Thermodynamic calculations

For thermodynamic calculations of the datasets the computer code WATEQ4F was used because a lot of U phases are added and its applicability in U prospections has been tested (Nordstrom *et al.*, 1979; Runnels and Lindberg, 1981).

The most widespread As mineral in the mine, loellingite (FeAs$_2$), is not added to the thermodynamic database. Nevertheless, since loellingite is oxidised to arsenolite (As$_2$O$_3$), which can be calculated by

WATEQ, arsenolite can be used for an assumption of loellingite–water interactions.

Uraninite and gummite are the phases with the highest saturations computed by WATEQ4F. Their saturation indices (log IAP/$k_T$) show a slight oversaturation and undersaturation, respectively. It is not yet clear, from the point of view of the saturation index, why the U content of the water increased and remains stable. The saturation index of the arsenolite saturation was very low in the beginning (−40) but it rose to −13 during the first year. Afterwards no significant change in the saturation index could be observed.

Calcium-ions buffer the SO$_4$, which is produced by sulphide oxidation partly catalysed by bacterial activity (Baas Becking *et al.*, 1960; Strasburger *et al.*, 1991), and results in the formation of gypsum. The calculation showed that the gypsum reaction is not yet in equilibrium and that the SO$_4$ mass concentration will increase until the saturation index will reach zero (Fig. 4).

### CONCLUSIONS

After nearly 4 a of flooding most of the constituents are increasing at a much slower rate, giving an apparent plateau, which could be confirmed by thermodynamic calculations of U- and As-phases. Oxidation of sulphides, catalysed by bacterial activity, increases the SO$_4$ mass concentration, but does not decrease the pH of the water. The mass concentrations

## gypsum saturation index
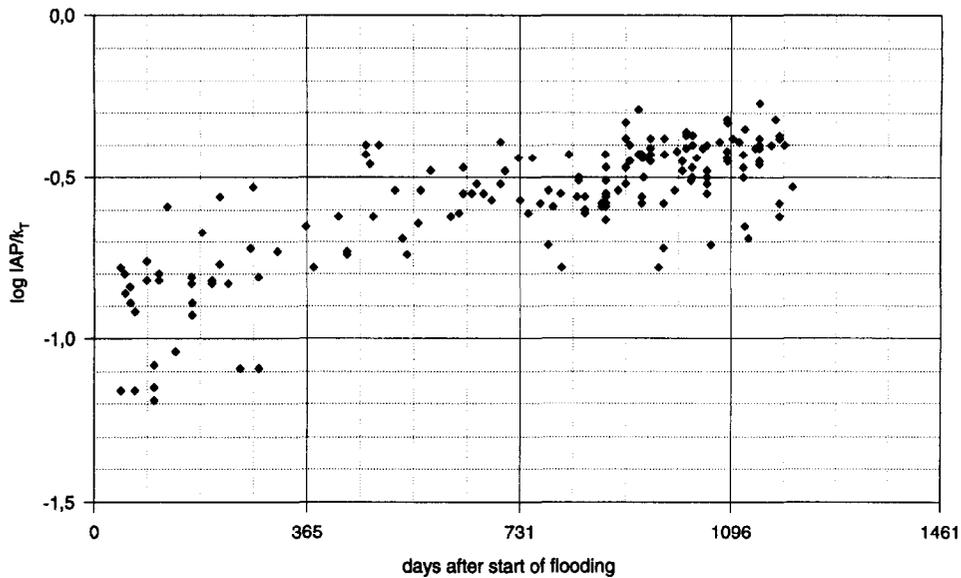


Fig. 4. Gypsum saturation index. Only results from flooding water analyses are plotted. 163 datapoints.

of important constituents of the flooding water are many times higher then those of the infiltration waters. Therefore, consideration should be given to separating infiltration waters from the flooding water by technical barriers to preclude the need for a treatment plant.

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